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Recent advances in fluorescence excitation spectroscopy have produced significant increases in detection sensitivity for single pentacene molecules in crystals of p-terphenyl at low temperatures. With the increased signal to noise ratio, we have observed two classes of pentacene behavior. While some pentacene defects have fixed, lifetime limited Lorentzian excitation line shapes (7.8 MHz FWHM), other pentacene defects exhibit spontaneous shifts in resonance frequency of up to 100

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by

W. P. Ambrose, T. Basche, and W. E. Moerner

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SINGLE MOLECULE SPECTRAL DIFFUSION IN A SOLID DETECTED VIA FLUORESCENCE SPECTROSCOPY

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ABSTRACT:

Recent advances in fluorescence excitation spectroscopy have produced significant increases in detection sensitivity for single pentacene molecules in crystals of p-terphenyl at low temperatures. With the increased signal to noise ratio, we have observed two classes of pentacene behavior. While some pentacene defects have fixed, lifetime limited Lorentzian excitation line shapes (7.8 MHz FWHM), other pentacene defects exhibit spontaneous shifts in resonance frequency of up to 100 MHz. Residence times between spectral jumps are on the order of seconds to minutes at 1.5 K. Increasing the temperature from 1.5 to 6 K appears to produce a faster-than-linear increase in jump rate with temperature; we suggest single pentacene defect spectral diffusion is due to thermally assisted structural changes in the p-terphenyl environment.

I. INTRODUCTION

Recent advances in high-efficiency fluorescence excitation spectroscopy of pentacene in p-terphenyl crystals¹⁻³ have improved the signal to noise ratio for the detection of single pentacene defects, thus confirming single pentacene detection using absorption techniques.⁴ Using 1-10 μm thick crystals, tightly focused laser beams, and high collection efficiency, background emission is significantly reduced below the fluorescence emission rate of single pentacene defects. To observe single molecules, the laser is tuned out into the wings of the pentacene O_1 site inhomogeneous line until the number of defects per homogeneous linewidth is less than 1. With the improved detection sensitivity, we have observed two classes of pentacene defects present in both the red and blue wings of the inhomogeneous line: class I consist of stable, time-independent defects with lifetime limited homogeneous linewidths below 4 K, and class II have time varying resonance frequencies. Both classes of defects found in the wings of the O_1 site inhomogeneous line are found to have a Lorentzian low power line shape and thermal dephasing behavior characteristic of single, isolated pentacene defects in O_1 crystal sites.

II. EXPERIMENTAL DETAILS

Crystals of p-terphenyl lightly doped with pentacene (in the 10^{-6} to 10^{-9} mole/mole range) are grown by cosublimation. The resulting p-terphenyl crystal platelets have elongated hexagonal shapes, which are less than 10 μm thick and up to 7 mm wide. Crystal thicknesses are determined by measuring optical interference fringe spacings in a room temperature spectrometer. Pentacene concentrations are determined from optical absorption or emission spectra.

Samples are mounted on a fluorescence collection assembly consisting of a N.A. =

0.98 parabolic reflector and either a laser focusing lens or an optical fiber epoxied to the sample. A carbon resistor mounted near the sample serves as a thermometer for temperature dependent measurements. The sample optical assembly is inserted into a liquid helium optical immersion cryostat, and a tunable single frequency dye laser is focused into a sample with laser focal diameter of 5 μm full width at half maximum (FWHM). For these experiments, the laser is tuned into the wings of the O_1 site inhomogeneous line, which is centered at 592.321 nm. The O_1 site inhomogeneous linewidths in these thin crystals depends on strain introduced during handling, and varies from 2 to over 42 GHz (0.002 to 0.05 nm). The collected emission is long pass filtered and detected with a cooled GaAs photomultiplier tube.

III. RESULTS AND DISCUSSION

Figure 1 shows a time sequence of excitation spectra, which were obtained in a fixed laser focal spot. These spectra were obtained in a narrow frequency region (300 MHz) far into the wings of the inhomogeneous band of O_1 sites. The spectra contain three time-independent class I peaks, which form stable ridges along the time axis near -130, -70, and +10 MHz. The peaks have unequal sizes because of the different pentacene positions within the Gaussian laser focus, which is verified by moving the laser spot.² The 0 to 150 MHz region has a single class II defect whose frequency varies from one scan to the next. This same molecule can appear several times in the same 2 min. laser scan, or almost not at all. Notice that in the same $\sim 50 \mu\text{m}^3$ volume of crystal and at nearly the same frequency there are both class I defects as well as spectrally migrating class II defects. We broadly use the term "spectral diffusion" to refer to the changes in resonant frequency that occur as a function of time for class II single pentacene defects.

The linewidths of both class I and class II defects broaden with temperature and power. Fig. 2 shows the low power limited linewidth for individual pentacene molecules from 1.5 to 10 K. Below 4 K, these Lorentzian shaped excitation peaks attain a FWHM of 7.8 MHz.³ From 4 to 10 K, the linewidth rapidly broadens by a factor of 100 due to thermal dephasing of the optical transition. These results can be compared with previous photon echo experiments for ensembles of isolated pentacene molecules and dimers in p-terphenyl crystals.⁵⁻⁷ From photon echo experiments, the optical dephasing time temperature dependence was found to follow an exponential form described by thermal excitation of a single librational level.⁵ The dephasing behavior of each type of isolated defect and dimer site is different⁷ and can be used as a characteristic signature for these various pentacene defects. The solid curve in Fig. 2 is a fit with this form of dephasing. The lifetime limited linewidth (7.8 ± 0.2 MHz), librational energy (38 ± 1 K), and pure dephasing-time prefactor (9.5 ± 1 ps) are in agreement with previous results for large ensembles of isolated pentacene defects in O_1 sites.⁵⁻⁷

When the laser frequency is held constant near a time varying defect, the detected fluorescence turns on and off discontinuously as the molecule spectrally jumps into and out of resonance with the fixed laser frequency. Figure 3 shows that when the excitation power level is varied at a fixed frequency, the rate of spectral jumps does not appear to be influenced. The mean times between jumps in Fig. 3 (a) and (b) of 80 and 61 seconds do not decrease by the factor of 5.3 increase in the fluorescence excitation rate. Hence, the spectral jump rate does not appear to be influenced by the optical excitation rate and thus cannot be regarded as a light-induced process that can produce spectral hole burning. The change in resonant frequency for class II defects appears to be a spontaneous process at low temperatures.

The absence of fluorescence in Fig. 3 only means that the defect is not absorbing at the laser frequency. To follow the shifts in resonance frequency directly, we scanned the laser frequency more rapidly in order to measure the spectral position of the defect at 1 to 3 second intervals. A digital waveform recorder locates the peak in each scan and records this resonance frequency as a function of time, as in Fig. 4. Figure 4 (a) shows how the resonance frequency of a spectrally jumping class II defect evolves with time at a fixed temperature of 4.18 K. The optical transition energy appears to have a preferred set of values and performs spectral jumps between these values that are discontinuous on the 2.7 second time scale of the measurement in Fig. 4. The jumps are up to 100 MHz in size, which is extremely small when compared to the optical frequency $[(10^8 \text{ Hz})/(5 \times 10^{14} \text{ Hz}) = 2 \times 10^{-7}]$. The spectral jumping behavior is small even when compared with overall inhomogeneous broadening effects; The largest jumps are at most 1/20 of the narrowest inhomogeneous width in our crystals.

One important physical measurement that would help to identify the source of the spectral diffusion effect would be temperature dependence of the jump rate. Pieces of the 4.18 K data in Fig. 4 (a) are expanded in Fig. 4 (b) and (c) for comparison with the shorter trend at a higher temperature of 5.77 K (Fig. 4 (d)). For this single defect, the mean residence time between the largest jumps is 80 seconds at 4.18 K, and 40 seconds at 5.77 K. This defect was confined to a 300 MHz range for over 5000 seconds at 4.18 K. At 5.77 K the spectral range initially expanded to 400 MHz, and after the 800 second time interval shown in Fig. 4 (d), this defect began to diffuse rapidly outside this range to lower frequencies, and became confused with other single molecules. Other defects have been observed that display a wandering behavior rather than discrete jumping with long residence times in between. These defects also appear to have an increasing wandering rate and range with temperature.⁸

The results for both class I and class II defects does not support the observation of spectral hole-burning, i.e., photo-induced changes in resonance frequency. One is thus led to consider what might have been the source of spectral hole burning observed during the earlier study of statistical fine structure (SFS) for pentacene in p-terphenyl.⁹ The SFS studies utilized the powerful absorption technique of FM spectroscopy to observe the small spectral variations near the center of the inhomogeneous line on a zero background. In fact, the size of the observed spectral holes even after extended irradiation were on the order of 1 part in 1000 of the total absorption. One interpretation of this result is that of all the pentacene molecules with center frequencies within one homogeneous linewidth of the laser frequency, only 0.1 % had a photoinduced pathway leading to changes in resonance frequency.

If it is correct that only 0.1 % of all molecules can participate in hole-burning, then in the single molecule regime one might expect on average to find a molecule capable of light induced resonant frequency changes for only one in 1000 molecules, and to date, only several hundred single molecules have been studied in detail. It is therefore quite possible that specific single molecules will be found that clearly undergo photoinduced spectral changes.

In contrast to the scarcity of single molecules able to undergo hole-burning, the appearance of single molecules of pentacene in p-terphenyl which spontaneously change resonant frequency with time is much more common. This surprising observation of spectral jumping may be analogous to spectral diffusion processes that play a crucial role in the physics of glasses and other amorphous materials.¹⁰ Here, the single-molecule technique allows the spectral changes to be followed in real time for only one center, without any averaging over an inhomogeneous distribution that may obscure the effect. The spectral changes take many forms, from discontinuous jumping, to quasi-continuous wandering, to creeping towards line center in small

discontinuous jumps. Also, the fraction of spectrally diffusing molecules clearly increases with distance from the center of the inhomogeneous line.² Thus, the occurrence of class II defects appears to be associated with sites that have some degree of local disorder so that the local strain or electric field is far from the equilibrium value.

Since the resonance frequency of a single molecule in a solid is extremely sensitive to the local strain (and other local fields) at the position of the molecule, the spectral jumps may occur because the class II pentacene molecules are coupled to an (unidentified at present) set of degrees of freedom in the nearby host crystal that are excited at 1.5 K. Further, these degrees of freedom interact with phonons, as evidenced by the increase in jumping rate and range at higher temperatures. Unfortunately, the diversity of behavior observed has made a detailed determination of the spectral diffusion temperature dependence of questionable value at this time.

IV. CONCLUSIONS

Several pieces of evidence support the interpretation that the excitation peaks such as those in Fig. 1 belong to single pentacene molecules. As the laser is tuned into the wings of the O_1 inhomogeneous line, single Lorentzian shaped excitation peaks are found that have the linewidth and temperature dephasing behavior of isolated pentacene defects in O_1 crystal sites. The strength of the fluorescence emission is approximately that which would be expected for a single molecule; however, attempting to quantify this absolute determination of fluorescence strength to better than a factor of two or so is quite difficult. Because of the unique dephasing behavior, they are unlikely to be due to coupled pentacene defects such as pentacene dimers. The Lorentzian line shape discounts the possibility that the excitation peaks are due to small ensembles of isolated pentacene molecules with exactly the same center

frequency, since this would require the complete absence of inhomogeneous broadening for these spatially separated defects. Perhaps the strongest proof that the observed spectra represent single impurity species are the observations of discontinuous spectral jumping. If there were several different molecules at the same frequency experiencing stochastic perturbations in resonance frequency, such clear spectral jumps would wash out into an ill-defined broadening of the spectral profile, which is definitely not what is observed.

Possible sources for the class II behavior should reflect the fact that it is connected with disorder in the crystal. One possible source for the effect could be librational tunneling of the central phenyl ring of the nearby p-terphenyl molecules about the p-terphenyl molecular axis. At room temperature, the central phenyl rings librate,¹¹ and at low temperature, these rings are frozen into an ordered phase.¹² If the central phenyl rings were to freeze into differently oriented domains, then the domain walls could be regions of local disorder in which the central phenyl rings alternately switch between adjacent domains. The spectral diffusion effects reported here may therefore result from discrete librational motions of the central phenyl ring of p-terphenyl driven by phonon assisted tunneling¹³ in an asymmetric double well potential that has become allowed due to the local disorder. Other possible sources for the class II spectral diffusion may be postulated. Migration of He atoms, vacancies or anharmonic local modes¹⁴ may also occur in the disordered regions of the crystal.

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FIGURE CAPTIONS

Figure 1. Single pentacene defect fluorescence excitation spectra time dependence. Upper half: wire plot of individual spectra, lower half: contour plot of same data obtained with 2 min. per spectrum, laser power 1.5 nW, and 0 MHz detuning = 592.539 nm. The appearance of class I defects at negative detuning and class II defects at positive detunings has no significance. (After Ref. 2).

Figure 2. Single pentacene molecule linewidth broadening with temperature. Rectangles are linewidth data taken with a laser focusing lens for molecules with excitation wavelengths of 592.334 nm, 592.342 nm, and 592.592 nm. Circles are data taken with a sample attached to an optical fiber with an excitation wavelength of 592.370 nm. The solid line is a fit to the data as described in the text. The molecule near 592.592 nm is a class II defect and the remainder are class I.

Figure 3. Spectral jump rate power independence. Spectral jumps are observed in the fluorescence signal of a single pentacene defect with a fixed wavelength of 592.362 nm at laser powers of (a) 0.89 nW and (b) 36 nW. The single molecule emission rate increases by a factor of 5.3 (the (b) ordinate is increased by a factor of 5.3 for comparison) for the factor of 40 increase in excitation power; however, the jump rate is qualitatively unchanged. (After Ref.3).

Figure 4. Qualitative increase in spectral jump rate with temperature. Peak-frequency trends for a single class II pentacene defect near 592.410 nm wavelength at a temperature of 4.18 ± 0.04 K ((a), (b), and (c)), and at a higher temperature of 5.77 ± 0.02 K (d). (b) and (c) are the 0 to 800 second and 800 to 1600 second sections of the

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data in (a) expanded for comparison with the 0 to 800 second data at 5.77 K in (d). Note that the jump rate for the largest jumps at 5.77 K in (d) is nearly twice the jump rate at 4.18 K in (b) and (c).

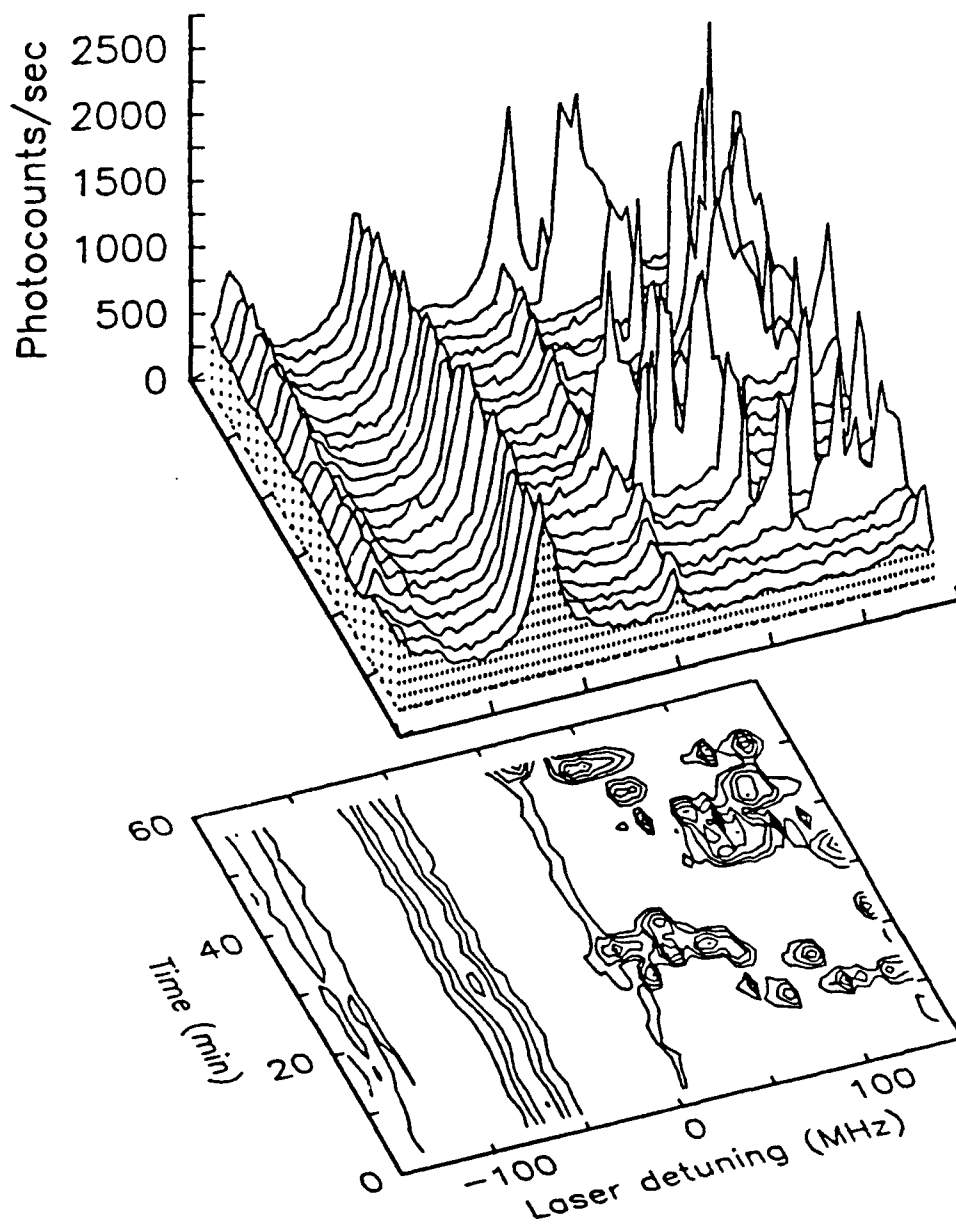


Figure 1

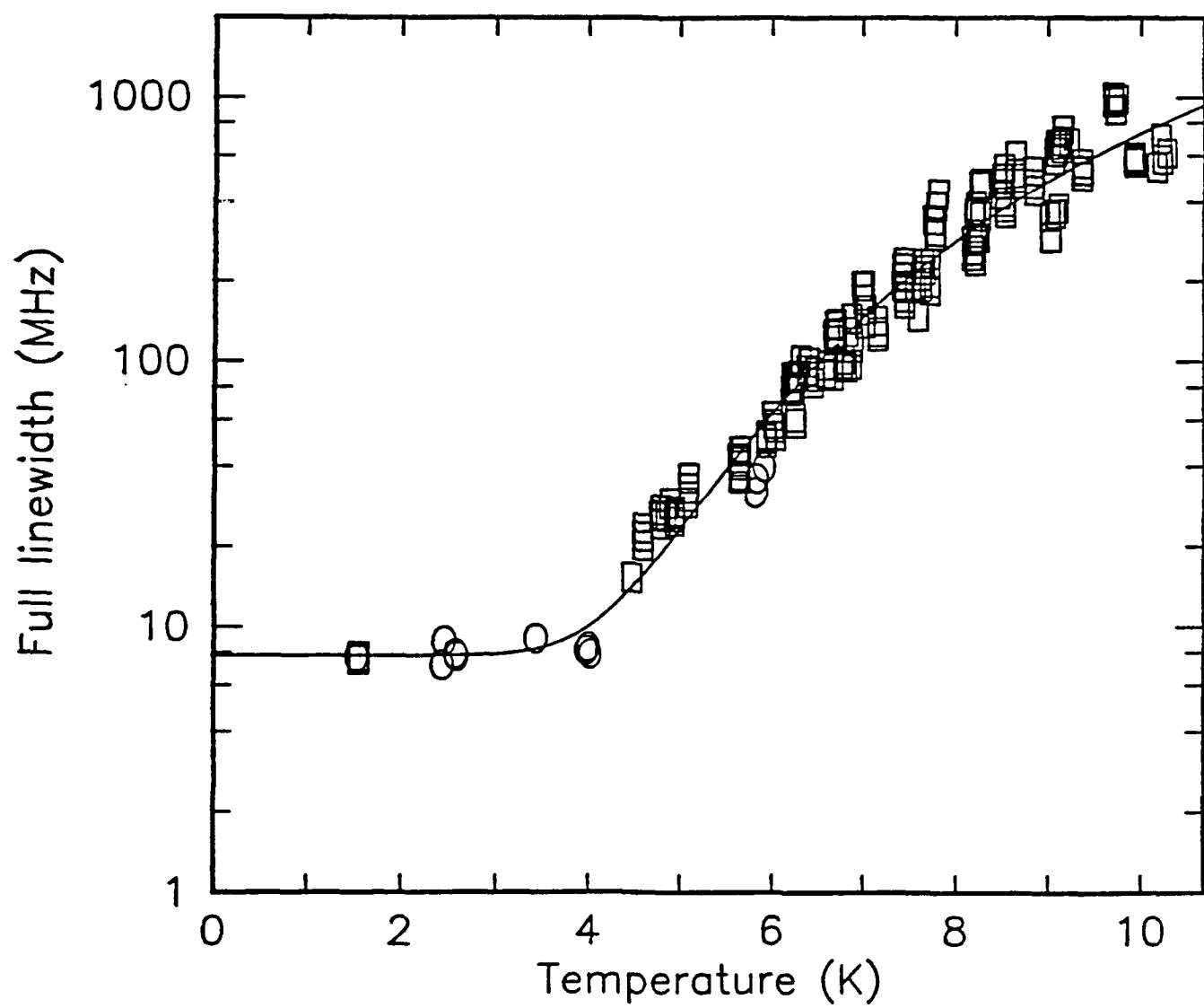


Figure 2

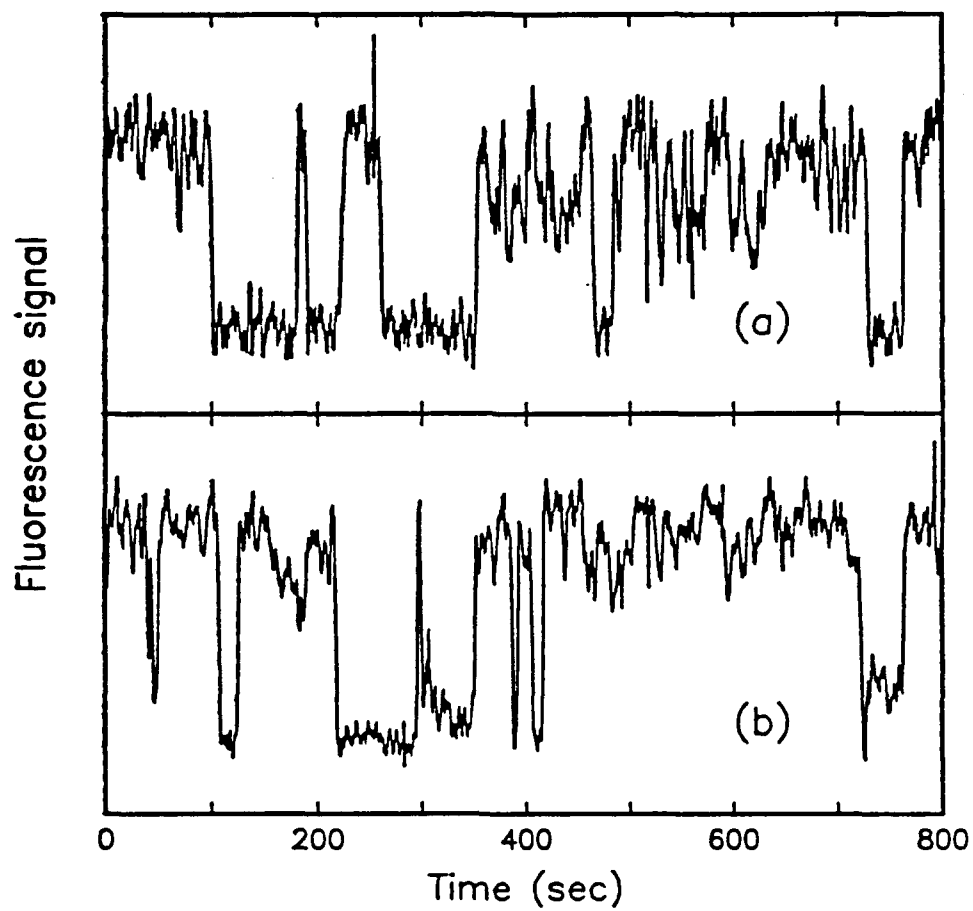


Figure 3

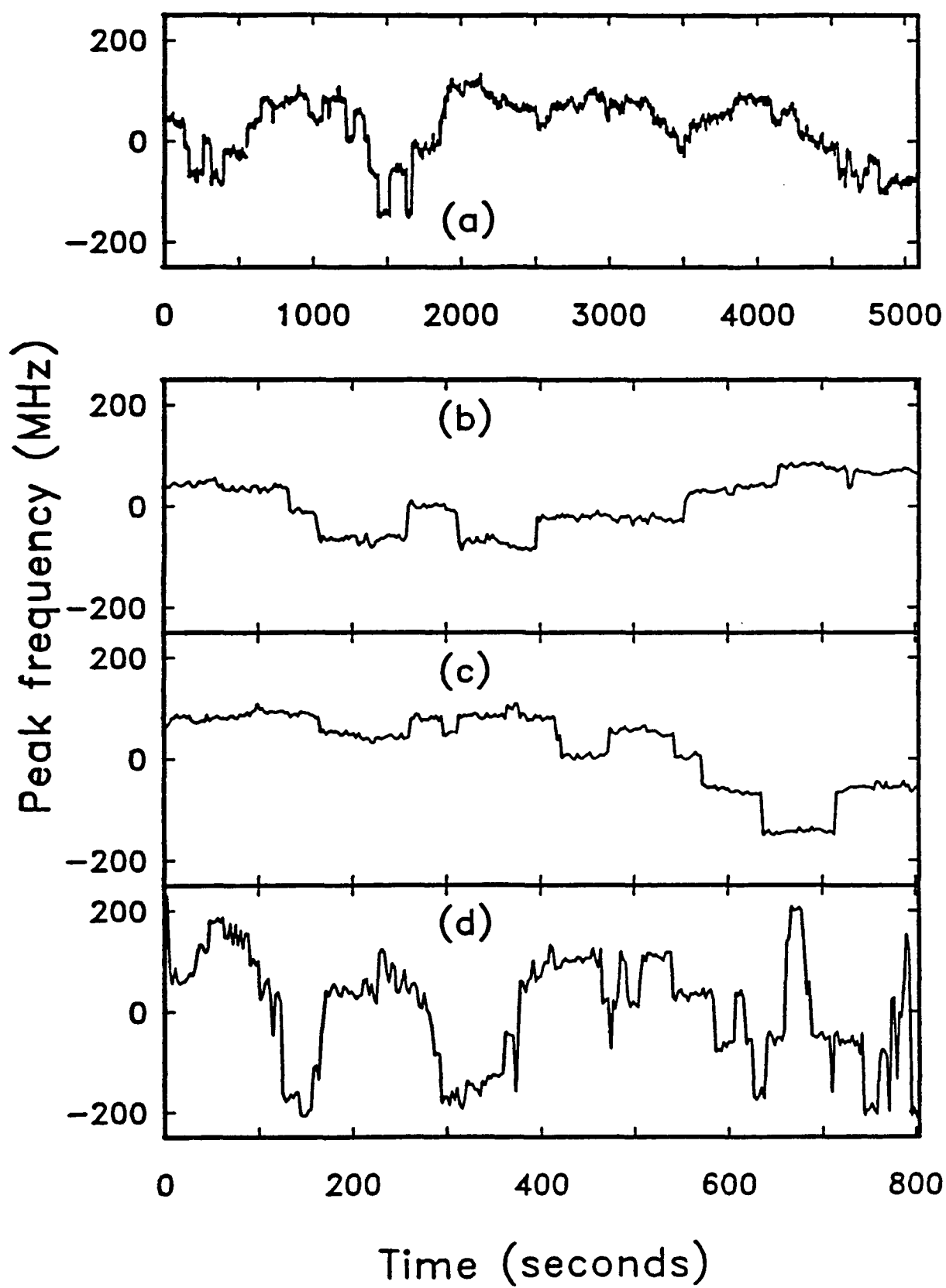


Figure 4

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